An Influence of Ga Content on Physical Parameters of Quaternary $Ge_{10}Se_{80-X}ga_xte_{10}$ Glasses

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Abstract - In the recent past, an adequate potential has been verified by so many distinguished researcher of gallium based and chalcogen enriched glassy alloys. In the present article, theoretical prediction of the effect of gallium on the physical parameters of $Se_{80-x}Ga_xTe_{10}Ge_{10}$ (x=3, 6, 9, 12, 15, 18, 21 at.%) like mean bond energy, glass transition temperature, heat of atomization and cohesive energy etc has been studied. It has been found that except the parameter R, all other parameters are found to increase with the increase in Ga content.

Keywords: Chalcogenide Glasses; Mean bond energy; Glass transition temperature; Cohesive Energy.

1. INTRODUCTION

The study of various properties on the basis of compositional dependency has been increased during last decade. Chalcogenide glasses S, Se, Te in binary and multi-component systems are promising materials for various electronic, optoelectronic, optical memory switching devices, optical recording media and photonic applications. As Se has unique property of reversible phase transformation Se based chalcogenide glasses have high transparency in the broad middle and far infrared region and have strong nonlinear properties. Recently various workers have reported the use of these materials for reversible optical recording using the amorphous to crystalline phase change [1-4].

Se are widely used for various applications in many fields as optical recording media because of their excellent laser writer sensitivity, xerography, and electrographic applications such as photo acceptors in photocopying and laser printing. It seems attractive, but pure selenium has disadvantage like short life time and low photo sensitivity. To overcome this problem, some impurity atoms like Ge, In, Bi, Te, Sb, Ag, etc. can be used to make alloys with Se, which may enhance sensitivity, crystallization temperature and reduce ageing effects [5-8].
The effect of an impurity in an amorphous semiconductor may be widely different, depending upon conduction mechanism and the structure of the material. While in crystalline semiconductors, the effect of a suitable impurity is always to provide a new donor or acceptor state, this is not essential in amorphous semiconductor. Instead of providing a localized impurity level in the mobility gap, an impurity may merely alter the mobility of the charge carriers or may introduce structural changes in the amorphous materials with or without modification of the localized states in the forbidden gap [9, 10].

The compositional dependence studies on glassy alloys were reported for Ge-Se, Ge-Se-As, Ge-Se-Ag, Ge-Se-Te, Ge-Se-Sb, Ge-Se-Bi [11-16]. Ge atoms act as bond modifiers thus they strengthen the average bond by cross-linking the Se chain structure, thereby enhancing the properties like glass transition temperature and resistivity. Ge-Se-Te system is a widely studied system and glass formation in this system occurs predominantly in alloys enriched with Se and containing 0-20 at % of Ga. Several researchers have studied the effect of in on the optical and electrical properties of chalcogenide materials. Addition of fourth element like Ga to Ge-Se-Te expands the glass forming region and also creates compositional and configurationally disorder in the system as well as induce large effect on their structural, physical, optical, electronic and thermal properties [17-19].

2. DEVIATION FROM THE STOICHIOMETRY OF COMPOSITION

The parameter R determines the deviation from stoichiometry and expressed by the ratio of content bond possibilities of chalcogen atoms to that of non-chalcogen atoms. For $Ge_{10}Se_{80-x}Ga_xTe_{10}$ system, the parameter R is given by [20, 21].

$$R = \frac{\beta N_{Se} + \delta N_{Te}}{\alpha N_{Ge} + \gamma N_{Ga}}$$

For R>1, the system is chalcogen rich, for R<1 system is chalcogen poor and R=1(point of existence of only hetropolar bonds) marks the minimum Selenium content at which a chemically network is possible without metal bond formation. From the figure 1 it is clear that our system is

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more chalcogen rich and turning towards chalcogen poor with increase in content of Ga in system.

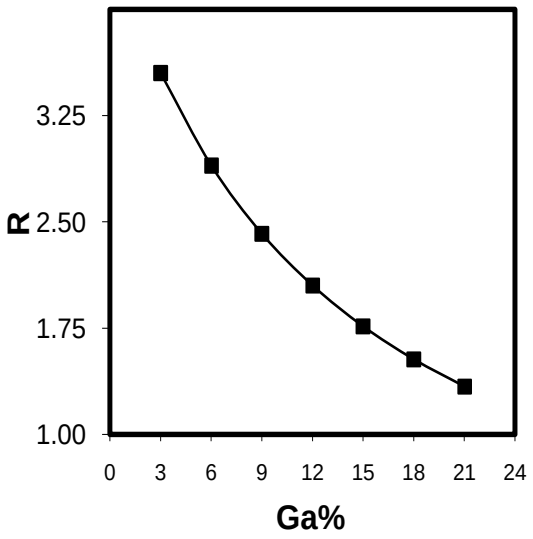

Figure 1: Variation of Parameter R with Ga content

3. CORRELATION BETWEEN MEAN BOND ENERGY AND GLASS TRANSITION TEMPERATURE

The properties of chalcogenide glasses are related to overall mean bond energy <E> which is the average function of average coordination number, the types of bond and bond energy. The correlation was proposed by TIchy & Ticha [22, 23]. The overall mean bond energy for the system $Ge_{10}Se_{80-x}Ga_xTe_{10}$ is given by

$$\langle E \rangle = Ec + Erm$$

where E_c is overall contribution towards bonds and E_{rm} is contribution arising from weaker bonds that remains after strong bond have been maximized i.e. average bond energy per atom if the "remaining matrix". For chalcogen rich system for R>1 where there are heteropolar bonds and chalcogen-chalcogen bonds

$$E = 4\alpha E_{Ge-Se} + 3\gamma E_{Ge-Ga} + 2\delta E_{Se-Te}$$

and

$$Erm = \frac{2\beta - 4\alpha - 3\gamma - 2\delta}{Z}$$

When R<1

$$E_c = \frac{2\beta\left(4\alpha E_{Ge-Se} + 3\gamma E_{Ge-Ga} + 2\delta E_{Se-Te}\right)}{4\alpha + 3\beta + 2\gamma}$$

The overall mean bond energy E for the glassy composition $Ge_{10}Se_{80-x}Ga_xTe_{10}$ (x=3, 6, 9, 12, 15, 18, 21 at %) is found to increase with increasing Ga content. A graphical variation of mean bond energy with atomic % age of Ga is shown in figure 2.

$$Erm = \frac{4\alpha + 3\gamma + 2\delta - 2\beta}{Z}\langle E \rangle$$

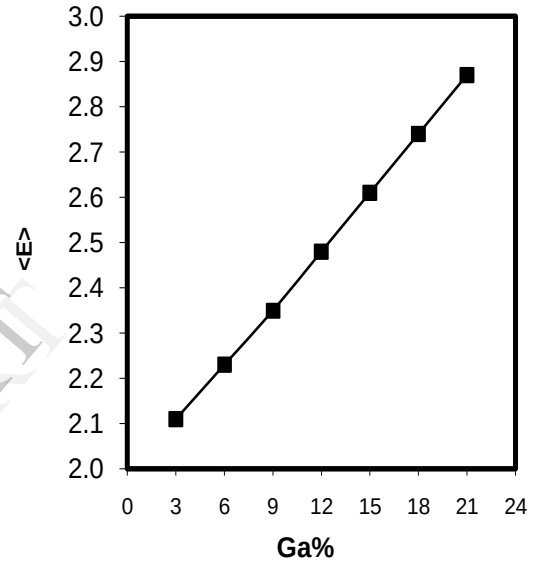

Figure 2: Variation of <E> with Ga content

The glass transition temperature (Tg), below which super cooled liquid becomes glassy alloy has been predicted theoretically for the composition by using two methods proposed by Tichy-Ticha and M.H.R. Lankhorst.

In first method Tichy and Ticha proposed an impressive relation between glass transition temperature and mean bond energy given by [24, 25].

$$T_g = 311\left(\langle E \rangle - 0.9\right)$$

A variation of glass transition temperature with atomic % age of Ga is shown in figure 3.

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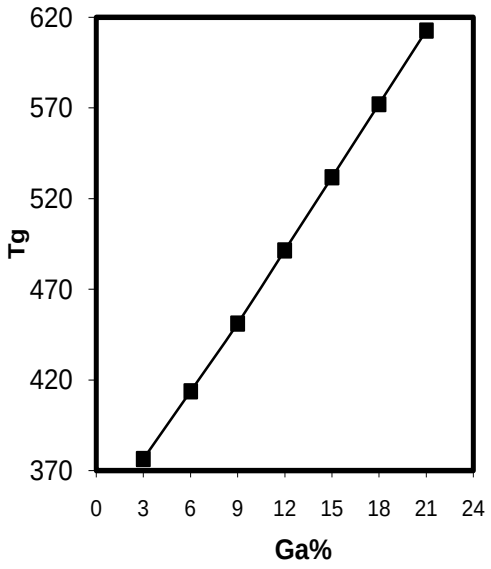

Figure 3: Variation of Glass Transition Temperature T_g with Ga content

4. HEAT OF ATOMIZATION

Heat of atomization or the enthalpy of atomization is the enthalpy change that is required for total separation of all atoms in a chemical compound such that the compound bonds are broken and component atoms are reduced to individual atoms. As proposed by Pauling [26], the heat of atomization H_s(A-B) at standard temperature and pressure of a binary semiconductor formed from atoms A and B is the sum of heat of formation ΔH and average heat of atomization Hs^A and Hs^B that corresponds to the average non-polar bond energy of the two atoms and is given by the relation

$$H_s\,(A\text{-}B) = \Delta H + \tfrac{1}{2}\,(H_s^{\,A} + H_s^{\,B})$$

The term ΔH given in the above Equation is proportional to the square of difference between the electro- negativities χ_A and χ_B of the two atoms.

$$\Delta H \alpha \left(\chi A - \chi_B\right)^2$$

In case of some materials for which it is found that the heat of atomization ΔH is about 10% of average heat of atomization and hence can be neglected. In the case of ternary and higher order semiconductor compounds, heat of atomization for quaternary compound can be written as

$$H_s = \frac{\alpha H_s^{Ge} + \beta H_s^{Se} + \gamma H_s^{Ga} + \delta H_s^{Te}}{\alpha + \beta + \gamma + \delta}$$

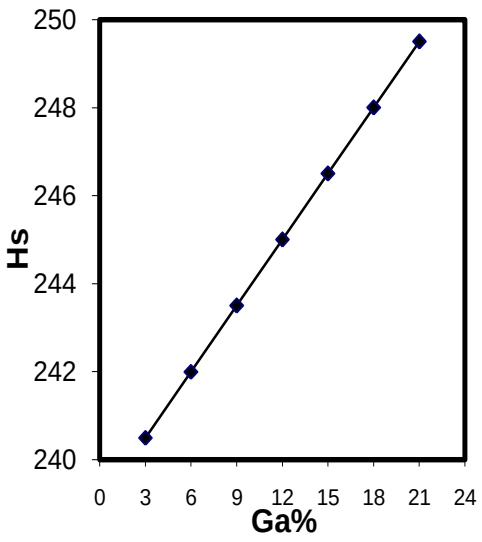

Figure 4: Variation of H_s with Ga content

where α, β, γ and δ are the atomic percentages of Ge, Se, Ga and Te. The value of heat of atomization for $Ge_{10}Se_{80-x}Ga_xTe_{10}$ (x=3, 6, 9, 12, 15, 18, 21 at %) chalcogenide glass are calculated**.** The variation of heat of atomization with increasing Ga content is shown in figure 4. It is clear from the figure that with the increase in atomic % age of Ga heat of atomization of the compound goes on decreasing. This can be explained as Ga content increases the number of Ga-Se bonds increase and Ge-Se bonds decrease. As the heat of atomization of Ga is less than Ge, so this lesser value of Ga decreases the heat of atomization of the network and hence the overall heat of atomization of the material decreases.

5. COHESIVE ENERGY

The cohesive energy of the system, defined as the stabilization energy of an infinitely large cluster of material per atom, has been calculated using the Chemical Bond Approach (CBA) [27]. According to CBA, atoms combine more favorably with atoms of different kind until all the available valences of the atom are filled. Bonds are always formed in the sequence of decreasing bond energies, which are assumed to be additive in nature. The heteropolar bond energies can be calculated by the relation [27],

$$E(A-B) = (E_{A-A} \times E_{B-B})^{0.5} + 30(\chi_A - \chi_B)^2$$

where E(A-A) and E(B-B) are the homopolar bond energies and χ_A and χ_B are corresponding electro negativities. The cohesive energy can be calculated using the relation [28],

$$CE = \sum_i C_i E_i$$

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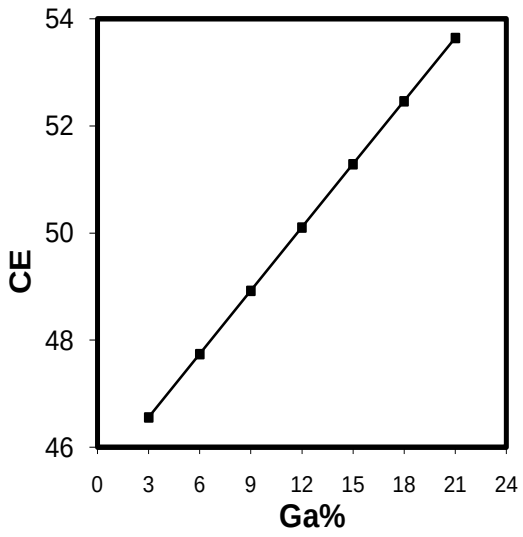

Figure 5: Variation of Cohesive Energy with Ga Content

where C_i is the distribution of the chemical bonds and E_i is the energy associated with the corresponding bonds From figure 5 it is evident that CE increases with increase in Ga from 3 to 21 at. %. Se atoms are strongly bonded to the Ge atoms and fill the available valences of the Te and Ga atoms respectively. But, still there are unsaturated Se atoms which appear as excess Se- Se bonds in the system. Thus, the overall bond energy of the system increases and hence the value of CE.

6. CONCLUSION

In the present work, important parameters viz. mean bond energy, glass transition temperature, heat of atomization and cohesive energy etc., have been calculated theoretically for $Ge_{10}Se_{80-x}Ga_xTe_{10}$ (x = 3, 6, 9, 12, 15, 18, 21 at. %) system. It has been concluded from various figures given above that the values of almost all the parameters vary linearly with variation in concentration of Ga from 3 to 21 at. %. The value of parameter R shows that our system is more or less chalcogen rich for all at % of Ga. The results here clearly depict variations in almost all parameters with increasing the content of Ga from 3 to 21 at % and hence confirming the status of above mentioned combination good for optical recording.

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